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INFLUENCE OF THE CHEMICAL STRUCTURE OF PHOSPHORUS-BASED EP ADDITIVES ON THEIR EFFECTIVENESS

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Translation of: "Einfluss der chemischen Struktur phosphorhaltiger EP-Additivs auf ihre Wirksamkeit," Schmierungstechnik, Volume 4, No. 12, pp. 372-377.

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16. Abstract

Investigations are reported on the influence of the structure of phosphorus-based additives and model substances on their effectiveness in low and high load regions in the four-ball apparatus. The results of four-ball apparatus runs with different stresses are compared with investigations on the reactivity of compounds with metals under thermal excitation under static conditions. It is shown that the wear-reducing effect at low loads (less than failure load) increases with decreasing reactivity of the compounds against iron within the region investigated. On the other hand, the four-ball apparatus welding load increases with increasing reactivity of the compounds to iron. The results were obtained by trial runs on the four-ball apparatus - an easily accessible device - and at present are valid only for this.

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INFLUENCE OF THE CHEMICAL STRUCTURE OF PHOSPHORUS-BASED EP ADDITIVES ON THEIR EFFECTIVENESS[1]

Weber, K., E. Eberhardt, and G. Keil[2]

Introduction /372*

Two previous publications [1, 2] reported the interaction between phosphorus-based EP additives and dynamic conditions. The results obtained already indicated that the reactivity of the phosphorus-based EP additives seemed to be the decisive factor in their effect as EP additives, as opposed to metals. This report now details the influence of the chemical structure of compounds containing phosphorus on their action in low and high stress regions, on the basis of experiments on the four-ball apparatus.

1. Experiments

The experiments were carried out with the following substances:

a) Tricresylphosphate (TCP): a product of the VEB Apolda Chemistry Laboratory (TGL 7601) purified by vacuum distillation, $n_{20} = 1.5587$.

b) O-dicresylphosphate (DCP): a product made according to Smith [3], $n_{20} = 1.5496$.

c) P-monocresylphosphate (MCP): a product made according to Rapp [4], melting point 115°C.

d) Triphenylphosphite (TPPit): a product from the VEB Chemical Industries, Greiz-Dölau, purified by vacuum distillation, $n_{20} = 1.5886$.

e) Diphenylphosphite (DPP): a product made according to [5], $n_{20} = 1.5548$.

f) Triphenylphosphate (TPPat): manufacturer: VEB Apolda Chemical Laboratory, melting point 49 to 50°C. /373

g) Orthophosphoric acid: a. p. manufacturer: VEB Apolda Chemical laboratories.

[1]Address to the 12th International Technology Symposium on Lubrication in Leipzig.
[2]VEB Schwedt Petrochemical Combine, Zeitz Combine Operation, Research Department (Official Director: Dr.-Ing. H. Roth).
*Numbers in the margin represent pagination in the foreign text.

h) Neutral oil I (NI), deparaffined and bleached, as basic oil.

i) Armco iron.

The conditions for the four-ball apparatus experiments were: balls of roller bearing steel, 100 Cr 6, speed of rotation 1400 rpm, stress $\leq$ 10 kp, time for wear behavior tests at light loads 30 min/load stage (due to the better differentiability), time for wear evaluation tests with heavy stresses 1 min/load stage.

The reaction with metal of the compounds used was monitored by ultrared spectroscope, using UR 10 made by VEB Carl Zeiss Jena. For this purpose, pickled plates of armco iron were heated in a solution of the additive in white oil and after given periods of time the reflection spectra of the resulting reaction products were recording. Electron-beam microanalytic measurements were carried out with the JXA-3A electron-beam microanalyzer (made by JEOL, Tokyo).[3]

2. Results

2.1 Analysis of Wear Mechanism in the Four-Ball Apparatus

2.1.1 Stresses Less than Failure Load

For this purpose, failure load is defined as that stress which, when exceeded, causes a sharp increase of wear intensity, brought about by a change in the wear mechanism.

Figure 1 shows the increase in wear mark diameter for NI, both non-alloyed and alloyed with TPPit, at stresses of 50 and 90 kp, as a function of time.

With scanning electron microscope investigations [6], it could be shown that with non-alloyed oil in an initial phase, which lasted only a few seconds, some parts of the contact surface became worn due to the high energy concentration, whereby adhesive wear occurred. Since, however, the contact surface

[3]We would like to thank Mr. Daebritz of the Dresden Technical University, Physics Department, Experimental Physics II, for carrying out the measurements.

available for wear is small, the energy used is sufficient to separate the welds. At the end of the initial phase the wear mechanism changes to mainly abrasive wear. When introduced into the four-ball apparatus, wear inhibitors suppressed the periods of adhesive wear and especially decreased the abrasive wear. The latter may be seen in Table 1, which shows the increase in wear marks for a non-alloyed oil and an oil alloyed with a wear inhibitor as a function of time.

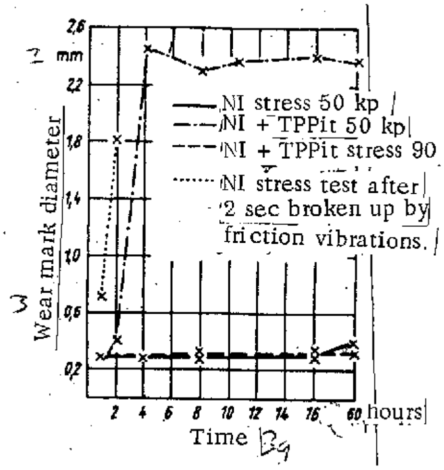


Figure 1. Wear Mark Diameter as a Function of Time.

Sample	Wear mark diam. after	
	1 min.	30 min.
NI	0.30 mm	0.80 mm
1.68% TPPit in NI	0.27 mm	0.50 mm

Table 1. Increase of Wear Mark Diameter with Time, Stress 40 kp.

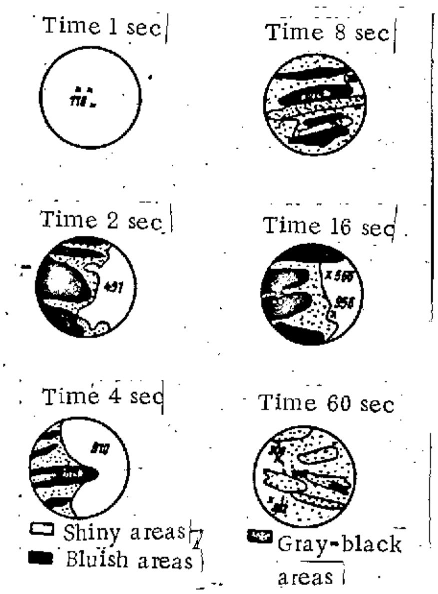


Figure 2. Phosphorus Concentration on Wear Marks as a Function of Time (NI + 2.52% TPPit, Stress 50 kp).

Figure 2 shows the result of electron-beam microanalytic investigations on the formation with time of a protective layer as the pre-condition for reduction in wear on the friction surfaces, brought about by the additive.

For better comprehension the wear marks are drawn in unit sizes. The /374 numerical values give the phosphorus impulses measured at these points every 30 seconds. It may be seen that the wear inhibitor builds up a protective layer (gradually at first) with increasing time by reacting with the metal, thus reducing the abrasive wear.

After formation of the protective layer, maximum wear reduction is attained when the rate of protective layer formation is exactly sufficient to replace continuously the reaction layers abraded during the friction process. This requires that the reactivity of the wear inhibitor must be exactly proportioned to the metal.

2.1.2 Stresses above the Failure Load

In the initial phase, which lasts only a few seconds [7], the energy concentration on the contact surface, which increases continously, is extremely high. Essentially two possibilities for the development of the wear process in the initial phase were observed:

a) the balls are welded due to extremely high energy concentration;

b) under favorable external conditions the high energy concentration is built up; it does not cause welding. Due to the high wear which occurs, the specific pressure declines as time progresses between the rapidly enlarging contact surfaces, the material stress drops off, and the wear mechanism then proceeds to chiefly abrasive wear.

An additive which should be active in the area over the failure load on the four-ball apparatus, must primarily impede welding of the balls in the initial phases. For this it is necessary for the additive to have a sufficiently high reactivity against the metal to form a protective layer rapidly enough. From investigations on EP additives containing sulfur, it is known that the reactivity against metals conforms with the activity of sulfides and disulfides in the four-ball apparatus [8, 9].

The following section will show, on the basis of investigations on phosphorus-based additives and model substances, which chemical structures best correspond to the general viewpoints derived in sections 2.1.1 and 2.1.2 for maximum /375 decrease in wear or EP effect. For this purpose the results of four-ball apparatus runs with various stresses were compared with investigations on the reactivity of the substances against metals under static conditions.

2.2 Results of Four-Ball Apparatus Test

The concentration of the additive solution was chosen such that the phosphorus content was the same in all solutions with the same running time. For the 30-minute runs oil with 0.168% phosphorus by mass was used, and for the one-minute runs oil with 0.252% phosphorus by mass. The results are shown in Figure 3 and Table 2.

2.3 Results of Ultrared Spectroscopic Investigations

Figure 4 shows the spectra of the reaction products of the substances investigated with iron surfaces with thermal excitation of oil and metal. The increase in surface concentration of the reaction product on the metal surface is calculated as a function of time using the increase in extinction of the bands characteristic of the reaction product (shown in Figure 4 by arrows). The results are compiled in Figure 5.

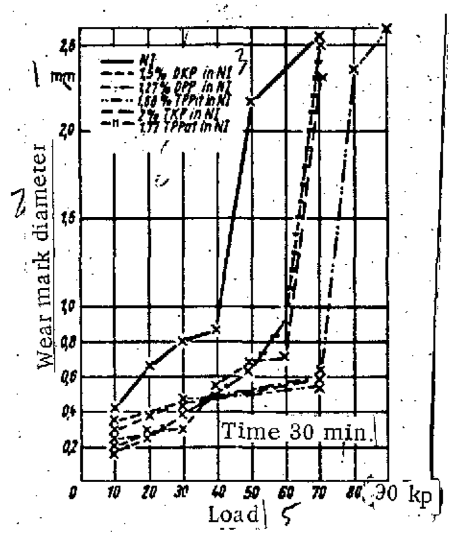
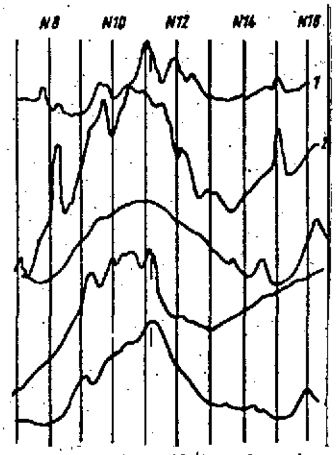


Figure 3. Wear Behavior of Phosphorus Compounds in the Four-Ball Apparatus.



1. 2.25% DCP in white oil/Fe, heating time 20 h.
2. MCP/Fe, heating time 0.25 h.
3. H_3PO_4/Fe, heating time 2.5 h.
4. 1.91% DDP in white oil/Fe, heating time 1 h.
5. 2.52% TPPit in white oil/Fe, heating time 10.5 h

Figure 4. UR Spectra of the Additive/Iron Reaction Product at 100°C.

Sample	Failure load kp	Welding load kp
NI	50	120/140
3% TKP	70	120/140
2.25% DKP	80	120/160
1.53% MKP (not fully dissolved)	50	180/200
0.93% H_3PO_4 (not dissolved)	50	220/240
2.66% TPPat	70	120/140
2.52% TPPit	70	120/140
2.52% TPPit technical	100	160/180
1.91% DPP	120	180/200

Table 2. Results of Four-Ball Apparatus Runs with One Minute per Stress Stage.

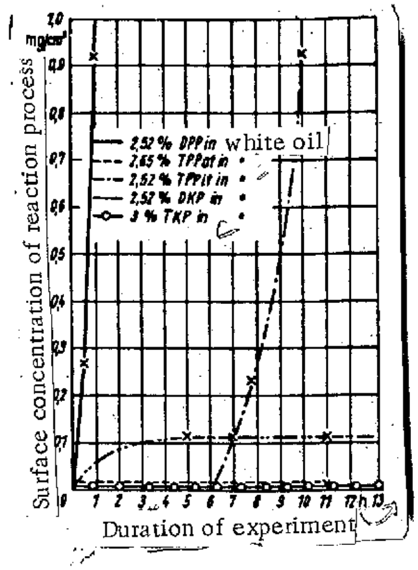


Figure 5. Increase of Additive/Iron Reaction Product on Iron Plates at 100°C as a Function of Duration of Experiment.

The spectra obtained for H_3PO_4 and MCP could only be evaluated qualitalively as they are insoluble in oil. With both compounds a reaction with the metal, shown by the ultrared spectroscope, was observed immediately after the iron had been brought to 100°C.

On the basis of the measurement results it can be estimated that the reactivity of the compounds introduced with respect to iron increases in the following order:

TCP, TPPat < TPPit < DCP < MCP, H_3PO_4, DPP.

The reaction observed after six hours between iron and the triphenylphosphite solution introduced can thus be attributed to the previous hydrolysis of TPPit in oil, giving rise to DPP.

3. Discussion of Results

3.1 With Stresses Under Failure Load

With stresses under the failure load, as has already been shown [2], protective layers are formed by a reaction between the phosphorus-based additive and the metal on the friction surfaces. The effect of the additive as a wear inhibitor is thus connected with a chemical action of the metal through the additive. Two possibilities suggest themselves to account for the different activities of the additives investigated:

a) Protective layers of different chemical composition are formed on the friction surface from the different additives. According to the different chemical structure, these layers have different physical properties, which are reflected in the different kinds of wear behavior.

b) The different reactivity of the additive with steel causes chemical action of different strengths on the friction surfaces.

With regard to a): For the following reasons it can be assumed, for the phosphorus-based additives investigated, that the reaction layers formed on the friction surfaces are always the same or very similar in their chemical composition and physical properties:

- With an additive concentration which corresponds to maximum decrease in wear, about the same decrease in wear is caused for all the additives investigated in the low-stress region (Figure 3). /376
- It appears from analytic investigations of the additive/metal reaction product with high thermal excitation that the same reaction products are formed from all additives.
- It can be shown directly by x-ray analysis of the attrition from four-ball apparatus runs that the same reaction products are formed from TCP and TPPit.

With regard to b): The reaction between additive and metal is the pre-condition for its effect as an antiwear additive, i.e. the original metal surface disintgrates; chemical wear occurs. In view of the chemical wear on the one hand and the anti-wear effect on the other, optimal effectiveness must be found. The target is the following: formation of a maximally effective protective layer with minimum chemical action on the metal. Figure 6 clarifies this with an example.

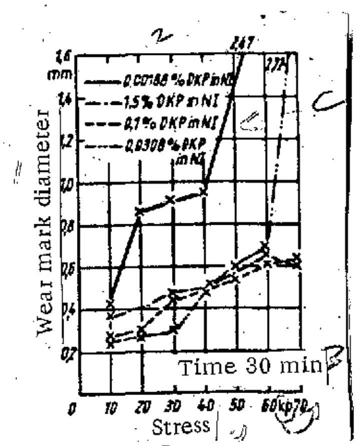


Figure 6. Wear Behavior of DCP Solutions in NI in the Four-Ball Apparatus as a Function of Concentration.

The wear is shown as a function of stress with different concentration of DCP in NI. It can clearly be seen that even at a stress of 40 kp a very slight additive concentration causes a maximum reduction in wear. With increasing additive concentration the wear also increases again, because there is additional chemical wear.

It results from the above that from a number of phosphorus-based compounds of different reactivity (provided the phosphorus concentration in oil is the same) with various friction conditions, only <u>one</u> compound with a very specific reactivity against metal can be optimally effective in reducing wear.

It may be expected that in the region of lower stresses those of the compounds investigated here which display only small reactivity to iron will be most effective. An evaluation of the oils investigated in respect of their wear-reducing effects is given in Table 3 for stresses between 10 and 70 kp.

Sample	Stress kp 10	20	30	40	70
NI	6	6	6	6	6
TKP	2	3	1	5	4
DKP	5	5	4	1	2
TPPat	1	1	3	4	5
TPPit	3	2	2	2	1
DPP	4	4	5	3	3

Table 3. Evaluation of the oils investigated with regard to their wear-reducing effects. 1 = maximum effect, 6 = minimum effect.

It can be seen that up to stresses of 30 kp the effectiveness of the oil decreases in the following order: TCP, TPPat > TPPit > DPP > DCP > NI. If we compare this with the order of increasing reactivity of the additive against iron (TPPat, TCP < TPPit < DCP < DPP) the result is that in fact the effectiveness of the additive as a wear inhibitor increases with decreasing reactivity against iron.

At a stress of 70 kp changes have occured in the evaluation of the additive such that the reaction compounds show greater effectiveness (cf. TPPat-DPP). The results show that, corresponding to the external conditions, here corresponding to the stresses, for each friction process up to the maximum wear reduction an additive with a very specific chemical reactivity is required.

3.2 Stresses Higher than the Failure Load

In this stress region, it is a question of the additive in the critical initial phase reacting immediately and intensively with the metal surface. For the phosphorus compounds investigated, we should hence expect that with in- /377
creasing reactivity of the compound the welding load would increase, analogously to the case with the sulfur compounds [8, 9]. Four-ball apparatus tests give the following series for the welding load:

NI, TCP, TPPat, TPPit < DCP, MCP, DPP < H_3PO_4.

The reactivity of the compounds investigated with iron decreases in the following order:

H_3PO_4, MCP, DPP > DCP > TPPit > TPPat, TCP > NI.

The comparison shows clearly that with increasing reactivity of the phosphorus compounds, the welding load increases.

Adsorption of the additive on the metal must be the prerequisite for the additive-metal reaction to take place. We would expect that the adsorption behavior of the additive would play an important part, particularly in the initial phase. The adhesion to mercury as a model metal was measured as a standard for the strength of adsorption. With the compounds investigated, the adhesion increases in the order TCP, TPPat ≤ TPPit < DCP < DPP, thus in conformity with the increase in reactivity against the metal. From this result, it is an open question whether the order is determined by the capacity to prevent wear by adsorption. However, due to the severity of the stress conditions in the four-ball apparatus, it is to be expected that the reactivity against the metal plays the dominant role.

The phosphorus concentration on the wear marks at the end of the trial run (load 100 kp) of some of the additives investigated could be measured with the aid of electron-beam microanalysis. This shows that the additives reacting with the metal generally also form thicker reaction layers on the friction surfaces.

4. Summary

Investigations are reported on the influence of the structure of phosphorus-based additives and model substances on their effectiveness in low and high load regions in the four-ball apparatus. The results of four-ball apparatus runs with different stresses are compared with investigations on the reactivity of compounds with metals under thermal excitation under static conditions. It is shown that the wear-reducing effect at low loads (less than failure load) increases with decreasing reactivity of the compounds against iron within the region investigated. On the other hand, the four-ball apparatus welding load increases with increasing reactivity of the compounds to iron. The results were obtained by trial runs on the four-ball apparatus - an easily accessible device - and at present are valid only for this.

However, it was concluded from the above that the parameters used in the test series led to comparable stress conditions and that under these conditions the relations are reproducible in influence on the wear process and can be deduced from the chemical properties of the compounds investigated.

It is necessary to analyze and interpret the physical and chemical parameters of the stress of the lubricant both in the laboratory and under practical conditions of application, whereby reliable criteria can be derived for transferring the relations determined in laboratory tests to actual practice.

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